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ISOTOPES — INDUSTRIAL TECHNOLOGY

(TID-4500)

FINAL REPORT

THE EFFECTS OF IONIZING RADIATION ON COLLOIDS

Period Covered: May, 1964 to November 1966

Prepared By:

The Research Department
UNIDYNAMICS/PHOENIX
A Division of UMC Industries, Inc.
Post Office Box 2990
Phoenix, Arizona 85002

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ABSTRACT

The Research Department of Unidynamics/Phoenix recently completed an experimental program under U. S. Atomic Energy Commission Contract No. AT(29-2)-1653. The broad scope of the program was a preliminary study of the effects of ionizing radiation on colloidal systems of special interest to various industries. Program goals were: (1) disclosure of radiation effects which might have industrial applications, and (2) selection of areas best suited for further, more critical study. Three colloidal systems and a class of chemicals used industrially to prepare emulsions were evaluated during the program.

The effects of gamma radiation on polyoxyethylene resins seem best explained by the assumption that two types of reactions, (chain scission and cross-linking and/or chain building) occur simultaneously, but at rates which are dependent on total dose, initial molecular weight and other variables. The scission reaction appears to be of only minor importance in the case of lower-molecular weight polymers (i.e. Carbowax 20,000). However, it is rapid in the higher molecular weight polymers (i.e. Polyox WSR-301).

With high molecular weight resins, chain scission appears to be independent of dose rate. Cross linking is characterized by a long induction period prior to manifestation of the effect, and the critical dose is dependent upon initial chain length and concentration. Cross linking was apparently not initiated until the concentration of fragments generated by chain scission reached a critical threshold value.

It is possible to suppress cross linking, however, by the introduction of oxygen prior to or during irradiation. The continuing drop in viscosity in the presence of oxygen is clear evidence of continued scission. This suggests that the radicals necessary for cross linking are scavenged by that gas. Once initiated, cross linking is rapid, confirming the supposition that a specific concentration of certain scission products is necessary to trigger and sustain the reaction. Data in hand permits no more than speculation regarding the reactions leading to the effects observed. Consequently, no definitive mechanisms are proposed at this time.

Exposure to ionizing radiation results in changes in the basic properties of a model aqueous colloid system. The most significant change in those properties studied was the relative stability of irradiated sols. In a "pure" system, irradiation increased the stability of the suspension to flocculation by alum. In the presence of sucrose, however, the relative stability of the suspensions was decreased. These changes in sol stability were observed after exposure to relatively low (less than 10^3 Rad) total doses.

The data indicates that it is possible to increase the sedimentation rate of an aqueous colloidal suspension and reaffirms previous work suggesting that this phenomenon may have application to water treatment problems. It is necessary to irradiate the suspensions in the presence of the flocculating agent to obtain this decreased stability, however, and the data shows that organic flocculants are ineffective after irradiation, presumably because of the radiation damage incurred.

Test data indicate that surfactant-free oil and water emulsions can be stabilized by irradiation. The stabilization occurs only when emulsification and irradiation are performed simultaneously, suggesting that a hydrophilic site is formed on one end of the oil molecule by reaction with radiolytic products in the water. This attack would be nil in separated oil and water. The pattern of viscosity changes observed in irradiated oils supported this hypotheses.

The potential industrial applications of radiation for the control of emulsion stabilities would seem to be greatest in the insecticide, paint, pharmaceutical and chemical industries.

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INTRODUCTION

Studies of the effects of gamma radiation on aqueous colloidal systems and their separate components have been performed. The systems studied included:

- (1) Sols of industrially important polymers
- (2) Preparations of a model suspensoid
- (3) Natural oils and their emulsions
- (4) Non-ionic surfactants.

Investigations demonstrated profound changes in the rheological properties of polyethylene oxide, polyvinyl alcohol and several other water soluble polymers. The bulk of the data deals with the radio-induction of precipitous decreases in the viscosity of dilute solutions of high molecular weight polyethylene oxides, and the gelation of those solutions at higher doses. Initial viscosity decreases occurred at total doses as low as those known to be biologically effective. It was not possible, however, to demonstrate changes in the irradiated polymers by the chemical methods employed.

The stability of suspensions of bentonite clay was affected by exposure to radiation. In the presence of an organic flocculant (sucrose), all irradiated suspensions were significantly less stable than controls. The effect was reversed, however, in suspensions to which no sucrose had been added.

Data obtained indicated that it may be possible to radiation-stabilize oil and water emulsions without the use of additives. Emulsification and irradiation must be performed simultaneously.

There were significant radiation-induced changes in the emulsifying abilities and chemical structures of certain commercial non-ionic surfactants. These changes were not related to any of the analytical procedures employed. The studies were preliminary, however, and the preparations investigated are known to be heterogenous. Modifications in the test procedures would probably permit accurate definition of the nature of the irradiation-induced changes.

The areas of investigation outlined above are more fully discussed in subsequent sections, and the following section contains a description of the irradiation facilities employed for these studies.

FIGURE 1
1,200 CURIE SOURCE

IRRADIATION FACILITIES

A 1,200 curie cobalt-60 irradiator was used throughout the majority of the program. Later, during the last three months of the program, an 8,000 curie cobalt-60 irradiator became available. This new facility is highly flexible and offers potential for future investigations. In addition to the two irradiation facilities, a stirring apparatus was designed for the study of irradiation effects under dynamic conditions. These three items are discussed in subsequent paragraphs.

1,200 Curie Irradiator. A nominal 1,200 curies of cobalt-60 was used as the source of gamma radiation for the initial studies. This source was designed, installed and initially calibrated using the Fricke ferrous-ferric ion dosimeter under AEC contract No. AT(11-1)-905.

Calibration procedures are detailed in UMC Document No. D63-341⁽¹⁾. Figure 1 on the opposite page presents a schematic of the source and a plan view of the sample tray.

Samples were irradiated by lowering the tray to any of several known points, indexed on the support cables, and raising the source out of the storage safe to a fixed position. Figure 2 is a graph of the gamma field vertical distribution at the beginning of the period covered by this report.

(1) AEC Report No. COO-275: *Investigation of the Effects of Ionizing Radiation on Synthetic Detergents, Sewage Collodial Characteristics and Sewage Sedimentation* (Unidynamics/Phoenix Document No. D63-341, 6 September 1965).

NOTES:

- 1) 2,000-Curie Nominal Cobalt-60 Source
- 2) Measurements by Fricke Ferrous-Ferric Sulfate Dosimeter
- 3) Date: March 18, 1964

FIGURE 2

VERTICAL GAMMA FIELD DISTRIBUTION
ABOUT SOURCE GUIDE TUBE

Prior to beginning experimental work on the subject contract, and at appropriate intervals thereafter, the source was recalibrated using the method mentioned above. The decrease observed in the intensity of the gamma fields was in accord with that expected from radioactive decay.

8,000 Curie Irradiator. In June, 1966 the Research Department began operating an irradiator containing 8,000 curies of cobalt-60. The facility consists of a subterranean room approximately 20 feet by 10 feet and roofed with approximately 3.5 feet of concrete. Access to the room is gained by entering a single door equipped with appropriate interlocks.

The radioactive material, 12 standard strip sources obtained from Brookhaven National Laboratories, is stored at the bottom of a pool of water 16 feet deep and approximately 4 feet in diameter. To perform irradiations in air or on samples exposed to other atmospheres, targets are positioned at appropriate points near the pool, and the radioactive material is raised from the pool by a rack and pinion assembly. Provisions have been made to permit variation of the geometry as well as the number of strips to which any sample is exposed.

Preliminary dosimetric studies indicate that air dose rates approaching 10,000 rad/min, as an upper limit, are possible with the facility. With large or bulky samples, this optimum is reduced by an order of magnitude. The lower limit of dose rate has not been ascertained, but the flexibility of the facility insures that a broad range of dose rates will be attainable.

Equipment for Study of Radiation Effects in Dynamic Systems.

Apparatus was designed and fabricated for the study of radiation effects on clay suspensions under dynamic conditions. The apparatus consisted of seven ganged paddles driven by a single rheostatically controlled electric motor. Paddles were spaced approximately four inches apart and arranged in semicircular fashion to permit simultaneous studies at a single dose rate, or at multiple dose rates.

The paddles and shafts were originally fabricated of stainless steel, but serious corrosion problems were encountered. Coating these parts with nylon was not permanently effective in reducing corrosion, and it ultimately became necessary to fabricate the paddles and shafts from plexiglass. These paddles were 2 by 1.25 inches and were perforated to allow the agitation of approximately 50 percent of the total volume when submerged into a sample held in a 100 milliliter low form graduated cylinder. There were fourteen perforations (approximately 3 millimeters diameter) in each paddle. This configuration permitted even flow of the liquid through the paddles during agitation as well as flocculation growth during slow-mix cycles.

Routine calibration of rheostat setting vs. revolutions/
unit time was performed to facilitate corrections for wear
in the gear train and shafts.

WATER SOLUBLE POLYMERS

Introduction. Available literature contains many reports on the effect of ionizing radiation on the polymerization of various monomers, on grafting reactions and on the aging of polymeric structures. There has, however, been little investigation of the effect of ionizing radiation on aqueous solutions of water-soluble polymers. Most of the reports which have appeared were concerned primarily with the further polymerization and cross-linking leading to sol gelation.

The wide variety of natural and synthetic water-soluble polymers currently of industrial interest may be classified as follows:

- (1) Polymeric ethers
 - a. Low Molecular Weight (Carbowax)
 - b. High Molecular Weight (Polyox)
- (2) Polysaccharides
 - a. Natural or unmodified
 - i. Guar gum
 - ii. Gum Acacia
 - iii. Pectins
 - iv. Extracts of Irish Moss, etc.
 - b. Modified cellulose
 - i. Methylcellulose
 - ii. Hydroxyethylcellulose
 - iii. Carboxymethylcellulose
- (3) Polyvinyl products
 - a. Polyvinyl alcohols
 - b. Polyvinylpyrrolidones

FIGURE 3
 EFFECTS OF IRRADIATION ON VISCOSITY OF AQUEOUS 1% POLYMER SOLUTIONS

Most of these materials are produced by a number of manufacturers in various grades. Differentiation between grade may be on a basis of molecular weight, purity (edible, non-edible, pharmaceutical, etc.), particle size, end-group modification and similar criteria. The materials are used alone or in combination as emulsifying agents, thickeners, gelants or thixotropic agents in water-based paints, ice cream, pharmaceutical products, cosmetics, polishes and a multitude of other products.

In the United States, several million pounds of these materials are used annually. When employing these preparations, the properties of a finished product are controllable only by selection of polymer grade and/or concentration. The use of gamma irradiation offers promise as a third means of control in suitable systems. Preliminary experimentation using relatively unsophisticated equipment for measurement of viscosity indicated that the viscosity of solutions of certain water-soluble polymers could be radically changed by irradiation (Figure 3).

Depending upon the use, Newtonian, pseudo-plastic or dilatant character may be desired in a product. The equipment used in our preliminary experiments did not, however, permit sophisticated rheological measurements. A Brookfield model RVT viscometer was used to obtain such data. This instrument characterizes the rheological properties of solutions by measurement of viscosity over a range of shear conditions.

Equipment Setup. To permit irradiation of the solutions in rigorously controlled atmospheres, gas washing bottles (Kimax #15060 or Corning #1760) were used as reaction vessels. These

were connected with a pressure vessel so that a slow, continuous flow of gas (nitrogen or oxygen) could be maintained during the radiation process. Figure 4 illustrates the equipment used, and the standard positions of the reaction vessels with respect to the source.

Initially in the current study, a scheme of serial irradiation was used. That is, reaction vessels were charged with the solution to be irradiated. These vessels were placed into the source well at positions where the dose rate was appropriate. They were then irradiated for the desired time. The vessels were next removed from the source, and the pH and viscosity were measured. Solutions were then returned to the vessels for continued irradiation.

When the 8,000 curie source was placed into operation (Monthly Letter Report #11), it was possible to discontinue this procedure because of the improved facilities. Subsequent to that time, replicate samples of the same solution were irradiated at each dose rate. After accumulating a given total dose, the irradiation was discontinued, one of the samples was removed for study, and irradiation of the remaining undisturbed samples was continued. Control solutions were maintained outside the radiation field under conditions similar to those of the experimental solutions.

Viscosity measurements were made with a Brookfield viscometer using a spindle appropriate to the viscosity of the solution. To differentiate between Newtonian, pseudo-plastic, and dilatant materials, all viscosity measurements were taken over a range of spindle speeds. To detect thixotropy, measurements were made in

FIGURE 4 (*Sheet 1 of 2*)
STANDARD IRRADIATION POSITIONS

FIGURE 4 (Sheet 2 of 2)

STANDARD IRRADIATION POSITIONS

descending as well as ascending order of spindle speeds. During the early part of this investigation, a Brookfield Model RVF viscometer with a 1-log (2 to 20 RPM) range of spindle speeds was used. The instrument did not appear to be as versatile as required and was exchanged for a Model RVT instrument having slightly more than a two log (0.5 to 100 RPM) range of spindle speeds. The spindles used for these two instruments are identical.

Measurements of pH were made with a Beckman Model G Research pH meter. This instrument was standardized each day with appropriate buffer solutions.

Samples of control and irradiated sols were lyophilized and stored for later chemical analysis. Because of the hygroscopic nature of the materials, all samples were dried in a vacuum to constant weight over Drierite at 30° C just prior to analysis. Determinations of acetylation number, acid number and aldehyde groups were made by standard AOAC methods.

For determination of infra-red absorption spectra, films were prepared by drying the solutions on microscope slides. The films were examined using a Beckman IR-8 infra-red spectrophotometer.

All irradiations were conducted in a nitrogen atmosphere unless otherwise noted. Water was prepared by re-distillation in a Pyrex glass apparatus under a stream of nitrogen. The water was

FIGURE 5
EFFECTS OF GAMMA RADIATION ON VISCOSITY OF 6% AQUEOUS
SOLUTIONS OF HIGH-MOLLECULAR-WEIGHT POLYVINYL ALCOHOL

stored under nitrogen until use. Preparation of solutions and determination of viscosity as well as irradiations were performed under a stream of nitrogen. The data is not, therefore, directly comparable to that reported by King.²

Polyvinyl Alcohol Tests. Two grades of polyvinyl alcohol (Borden Chemical Co.) were employed in this study. One was 99.5 percent hydrolyzed and is hereinafter designated as "low acetyl". The other was 88 percent hydrolyzed and is referred to as "high acetyl". Our observations on changes in viscosity in both grades are summarized in Figure 5. Little or no change in viscosity was observed until a dose of about 10^5 rads had accumulated and, in this respect, high acetyl PVA is somewhat more sensitive to irradiation than is low acetyl material. Conversely, high acetyl material is more resistant to radiation as measured by changes in pH of the solution.

Infra-red absorption spectra of polyvinyl alcohol films were prepared from irradiated and unirradiated material of high and low acetyl content. Correlation of the rather small changes in infra-red absorption with changes in chemical constitution has not been possible. Determinations of hydroxyl number and carbonyl groups show no significant differences between irradiated samples and controls. Changes in carboxyl content, however, were observed after irradiation of low-acetyl PVA as shown on the following page.

(2) Paul A. King, *The Preparation of an Intermediate Class of Polyethylene Oxide Resins* (Paper presented to American Chemical Society, Spring 1966).

<u>Total Absorbed Dose</u>	<u>Carboxyl Content</u>
1. 0 Rad (Control)	0.053 mEq/gm.
2. 0.4 Mrads	0.146 mEq/gm.
3. 1.4 Mrads	0.119 mEq/gm.

From these data, it appears that carboxyl groups are produced in the earlier stages of irradiation. At about the time of gelation, the carboxyl content appears to be reduced. It is possible that gelation of this polymer is due to cross-linking by esterification.

Polyethylene Oxide Tests. The polyethylene oxides comprise a large family of products of molecular weights ranging from 1.5×10^3 to 3×10^7 . The materials used in this study were commercial products obtained from Union Carbide Chemicals Corporation. Compounds with molecular weights below 10^5 are designated as "Carbowax", and those with higher molecular weights as "Polyox". Each compound is also given a numerical suffix which denotes the molecular weight of a Carbowax but which has no published significance for a Polyox.

Following a preliminary examination of several grades, three representative products were selected for investigation:

- (1) Carbowax 20,000, molecular weight 2×10^4
- (2) Polyox WSR-301, molecular weight 3×10^6
- (3) Polyox WSR-N-3000, molecular weight about 3×10^5

These materials are discussed in the following paragraphs.

NOTES:

- (1) Carbowax 20-M—Union Carbide Chemical Co., molecular weight: 15,000 to 20,000
- (2) Cobalt 60 Gamma Irradiation at 2 dose rates of Carbowax 20-M 10% (W/V) aqueous solution
- (3) Viscometry: Brookfield model RVF, spindle # 1 at $28.0^\circ\text{C} \pm 0.2^\circ$
- (4) Each point represents 1 irradiated sample
- (5) Unirradiated control viscosities

FIGURE 6

**IRRADIATION EFFECTS UPON HIGH MOLECULAR WEIGHT
POLYETHYLENE GLYCOL (CARBOWAX 20-M)**

- a. Carbowax 20,000 - Viscosity changes were observed after irradiation of 10 percent aqueous solutions of Carbowax 20,000 and are presented graphically in Figure 6. Only minor changes occurred prior to accumulation of a total dose of about 1.5×10^6 rads, at which time the sol gels. The gelation reaction of this material does not appear to be dose rate dependent, but is a function of concentration. Figure 6 indicates that the initially dilatant solutions becomes pseudoplastic after gelation.
- b. Polyox WSR-N-3000 - Figure 7 summarizes changes in viscosity observed after irradiation of solutions of Polyox WSR-N-3000 of various concentrations. The viscosity decreases upon irradiation, reaching a minimum in the range of 10^4 rads before increasing rather rapidly. Figure 7 also indicates the extent of radiation induced changes in one and four percent solutions of this polymer. At each concentration, the irradiated solutions began to acquire Newtonian properties.
- c. Polyox WSR-301 - The changes in viscosity and rheology of Polyox WSR-301 solutions exposed to gamma radiation are summarized in Figure 8. Under anaerobic conditions and at a dose rate of 935 rads per minute, gelation occurs at a total dose of about $2-5 \times 10^4$ rads at both concentrations studied. Initially all solutions were pseudoplastic but became dilatant upon irradiation. Under conditions of oxygen saturation the viscosity continued to decrease.

FIGURE 7

EFFECTS OF GAMMA RADIATION ON AQUEOUS SOLUTIONS OF POLYETHYLENE OXIDE (WSR-N-3000)

VISCOSITY CHANGES IN 1% (W/V) AQUEOUS SOLUTIONS OF 2 DIFFERENT BLENDS OF WSR-301.

NOTES: (1) Dose rate was 186 rads/min.
 (2) Viscometry: spindle # 1, 28.0° C $\pm$ 0.20 and 20 RPM

FIGURE 8

EFFECTS OF GAMMA RADIATION ON AQUEOUS SOLUTION OF POLYETHYLENE OXIDE (WSR-39)

A comparison of the curves obtained for blends 3752 and 3804-20 indicates the lot-to-lot variance of this product. The differences in the initial viscosity of solutions prepared from the different blends confirms this lot-to-lot variability.

There appeared to be a dose rate dependent effect in the total dose required for gelation of this material. The data was inconclusive, however, and further evaluation of the observation is required before its true significance can be ascertained.

Conclusions. The effects of gamma radiation on polyoxyethylene resins seem best explained by the assumption that two types of reactions, (chain scission and cross-linking and/or chain building) occur simultaneously, but at rates which are dependent on total dose, initial molecular weight and other variables. The scission reaction appears to be of only minor importance in the case of lower-molecular weight polymers (i.e. Carbowax 20,000). However, it is rapid in the higher molecular weight polymers (i.e. Polyox WSR-301).

With high molecular weight resins, chain scission appears to be independent of dose rate. Cross linking is characterized by a long induction period prior to manifestation of the effect, and the critical dose is dependent upon initial chain length and concentration. Cross linking was apparently not initiated until the concentration of fragments generated by chain scission reached a critical threshold value.

It is possible to suppress cross linking, however, by the introduction of oxygen prior to or during irradiation (Figure 8). The continuing drop in viscosity in the presence of oxygen is clear evidence of continued scission. This suggests that the radicals necessary for cross linking are scavenged by that gas. Once initiated, cross linking is rapid, confirming the supposition that a specific concentration of certain scission products is necessary to trigger and sustain the reaction. Data in hand permits no more than speculation regarding the reactions leading to the effects observed. Consequently, no definitive mechanisms are proposed at this time.

AQUEOUS SUSPENSIONS

Introduction. A variety of colloidal suspensions are associated with many industrial processes. The suspensions may be aqueous or non-aqueous, organic or inorganic, desirable or undesirable. For the initial studies, suspensions of a montmorillonite clay of bentonitic origin were selected. This selection was based upon several factors:

- a. The properties of the clay are well-known, and it appeared to be uniquely suited for use as a model system.
- b. Bentonite clays are widely used as extenders, binders, thickeners, abrasives, etc., in the paint and pigment, rubber, petroleum, cosmetic, drug, ceramic, metal, construction, and insecticide industries.
- c. Bentonite clays are similar to the bulk of the suspended soil components in waste and natural ground waters.

Studies of radiation effects on both static and dynamic systems of these clays were undertaken.

Bentonite, strictly defined, is a natural rock formation composed of montmorillonite clays. The montmorillonite clays (e.g. montmorillonite, pyrophyllite, beidellite, saponite, etc.) are hydrated aluminosilicates resulting from the devitrification and chemical alteration of volcanic glass. In general, the composition of these clays is $\text{Al}_2\text{O}_3 \cdot (\text{SiO}_2)_n \cdot (\text{H}_2\text{O})_n$. The clays are platelike

crystals of micaceous habit and almost always contain considerable quantities of absorbed sodium, potassium, calcium and/or magnesium. In suspension, the montmorillonites are thixotropic, exhibit a high cation exchange capacity, and may be reversibly hydrated.

Through usage, the term bentonite has come to mean any of the montmorillonite clays. Material obtained from different vendors may have slightly different characteristics, largely dependent upon the original source of the clay (i.e. Rock River, Cheyenne, Dakota, Tennessee, etc.). The material used for the studies described below was obtained from two scientific supply houses. During experimentation, no significant difference was observed between the materials.

Two types of tests, static and dynamic, were conducted to allow observation of the following parameters:

(1) Static Irradiation Tests

- a. Zeta Potential
- b. Hydrogen Ion Concentration
- c. Conductivity
- d. Flocculation Value

(2) Dynamic Irradiation Tests

- a. Clarification with Inorganic Flocculants
- b. Effects of Sugar Impurity
- c. Clarification with Organic Flocculants

NOTE: DATA IS THE SAME AS FOR FIGURE 3

STANDARD CURVE

CORRELATION OF BENTONITE SUSPENSION CONCENTRATION
AND PERCENT TRANSMISSION OF SUSPENSION.

FIGURE 9
BENTONITE SUSPENSIONS

Both test setups and test results for the previous parameters are discussed individually in the following paragraphs.

Static Irradiation Tests. Stock suspensions of 325 mesh bentonite (E. H. Sargent Co., Fisher Scientific) were prepared in a Waring Blendor by slurring the desired quantity of clay (usually 10 grams) in 75 milliliters of distilled water. Before use, the specific conductance of the water was determined. If the reading obtained exceeded 1 ppm electrolyte as sodium chloride (equivalent to approximately 8.50×10^5 ohms/cm), the water was not used. After thorough mixing, the suspension was diluted to four liters with distilled water. The container was then stoppered and the material allowed to hydrate for at least 12 hours. At the end of the hydration period, the material was resuspended by shaking, and the larger particles were removed by two hours static sedimentation. The decanted supernatant was then diluted to the desired final concentration (0.06 percent unless otherwise stated) using distilled water.

The total solids in each suspension were estimated by measuring the optical density at 425 millimicrons with a Bausch and Lomb Spectronic 20 colorimeter and comparing this value with the standard curve shown in Figure 9. The curve was constructed by obtaining similar readings on various suspensions and determining the total solids in each of those suspensions by drying an aliquot to a constant weight at 100° C (Figure 9).

Measurements of zeta potential, pH, conductivity and flocculation value of suspension samples before and after exposure to Cobalt-60 gamma flux were taken as indices of radiation effects. Unirradiated control samples, treated in the same way as the test samples, were an integral part of every experiment. Irradiation was performed in stoppered test tubes (25 mm x 150 mm) or low form 100 milliliter graduated cylinders. All glassware was cleaned by soaking in chromic acid, washing in detergent, rinsing with hot tap water, and rinsing finally with distilled water.

Zeta Potential. Zeta potential is one measure of the electrokinetic charge surrounding the particles comprising a lyophobic suspensoid. The magnitude of this charge is directly proportional to the stability of the suspension, and it is used extensively in many industries as an index of this characteristic.³

Zeta potential measurements were performed using a Riddick type electrophoresis cell⁴ fabricated in this laboratory of acrylic plastic. The bore and length of the cell were 2.24 and 123.5 millimeters, respectively. The cell constant was calculated at 69.87, in close agreement with a value of 70 which is typical of such cells. Data was collected using the cell described, a DC power supply delivering 0 to 500 volts, a standard dissecting microscope, a microammeter (Simpson 260 VOM) and appropriate illumination.

(3) See bibliographical references 4, 5, 15, 16, 17, 19, 36, 43, 44, 50 and 54.

(4) R. H. Ottewill and R. F. Woodbridge, "Studies on the Electrokinetic Behaviour of Monodispersed Silver Halide Sols," *Journal of Colloid Science*, Vol. 19 (1964), pp 606 - 620.

FIGURE 10
CHANGES IN ZETA POTENTIAL OF BENTONITE SOLS
UPON GAMMA IRRADIATION - LOW DOSE RANGE

The initial data indicated that changes in the zeta potential of clay suspensions result from irradiation. These changes appeared to be cyclic in nature, oscillating in a somewhat regular pattern above and below the original value obtained. The changes appeared to be independent of dose rates between 125 and 620 rads per minute. Some contradictory data were obtained; however, these were ascribed to unsophisticated technique in determination of zeta potential. Figure 10 is typical of the early measurements obtained. These corroborate the data of Crowther.⁵

When the studies were extended to include higher total absorbed doses, anomalous data became the rule, rather than the exception. The oscillatory changes of zeta potential described above were obscured by unacceptably large variations in values obtained on control samples of irradiated material. Close control of experimental variables indicated that these variations were not attributable to such parameters as total solids of the suspensions, origin of the bentonite, impurities in the distilled water, pH or specific conductance of the sols. Continued investigation demonstrated that even data obtained at low total absorbed doses were subject to the referenced uncertainties because of variations in values of zeta potential within samples.

A total of 41 zeta potential determinations, each consisting of 20 or more particle mobility measurements, were performed on irradiated bentonite sols. Similar determinations were performed on 36 control samples. Statistical analysis of the data reflected

(5) See bibliographical references 15 through 19.

the referenced variations in zeta potential measurements within similar samples. The standard deviations of irradiated and control populations were quite wide, and it was not possible to statistically separate them.

Hydrogen Ion Concentration. Within broad limits, the pH of clay suspensoids exerts a profound effect on particle stability.

Because of this relationship, careful study of the pH of all experimental suspensions was undertaken. The measurements were performed in the standard manner with either a Beckman Zeromatic or Research instrument equipped with microelectrodes. All suspensions were mixed by inversion just prior to measurement of pH, and the pH of the distilled water used to prepare all stock sols was 6.2 ± 0.3 .

In spite of the precautions taken to prepare each stock suspension in an identical manner, the initial pH observed for these sols ranged between 6.8 and 8.7. Invariably, this initial value shifted downward as the sols aged. The magnitude of the shift ranged from 0.2 to 0.7 units. The shift was always approximately linear with the age of the sol, but the magnitude of the drift did not appear to be related in any way with any of the experimental parameters studied. The largest shift observed occurred over a period of seven days. This shift was 0.7 units in magnitude.

The pH of bentonite sols and distilled water samples subjected to irradiation was generally lower, by approximately 0.2 to 0.5 units, than corresponding unirradiated controls. Decrease in pH

dose rate was independent and approximately linear for the first few thousand rads, after which time it appeared to stabilize at a constant value of 0.5 units.

This pattern was continually modulated, however, by the occurrence of pH values substantially lower than expected in irradiated suspensions. These "anomalous" values were sometimes as great as 1.8 units below the expected, but were more usually in the order of 0.5 units. The readings were initially ascribed to poor technique, since it was never possible to confirm the value on a second sample taken immediately after the first, and these low values were totally incompatible with the remainder of the data.

However, similar readings were obtained sporadically for the duration of the study. The persistence of the observations, coupled with the fact that similar phenomena were never noted in control suspensions or irradiated distilled water samples, made it impossible to continue explanation of the "discrepancies" on the basis of an error in technique. Careful analysis of data, sampling methods, measurement techniques, etc., indicated that the variations could not be ascribed to impure distilled water, suspension preparation or age, errors in manipulation or method, or faulty instrumentation.

Although the occurrence of the anomalous readings was ubiquitous and could not be related to total absorbed dose from the available data, the majority of the reductions in pH were observed after

FIGURE 11
CHANGE IN CONDUCTIVITY IN IRRADIATED SAMPLES OF
BENTONITE SUSPENSIONS AND DISTILLED WATER

the samples had received more than 8,000 but less than 20,000 rads. The shifts observed also tended to be of greater magnitude in suspensions of high initial alkalinity (pH = 8.0 or greater) than in those with an initial pH which was either neutral or slightly acidic.

Conductivity. Because of the effect which solution conductivity may exert upon the electrophoretic characteristics of a clay suspension, measurement of this parameter was included as part of the subject study. The Riddick microelectrophoresis cell described previously was calibrated at a known voltage. This was accomplished by measurement of the current flowing when the cell was filled with a standard solution of potassium chloride. A cell constant of 360 was calculated from the data obtained using the relation below:

$$\text{cell constant} = \text{conductivity} \times \frac{E}{I}$$

Where: Conductivity = micromhos/cm

E = volts

I = microamperes

The conductivity of irradiated and control samples of both distilled water and bentonite suspensions was measured. Figure 11 is typical of the data obtained at dose rates of 180 and 250 rad/minute. It indicates that the conductivity of irradiated samples increases with increasing total dose. The data obtained

at higher dose rates was of limited continuity. However, a pattern similar to that operative at low dose rates was indicated.

Flocculation Value. This characteristic of suspensoids is a universally accepted measure of stability. For purposes of this study, flocculation value was defined as the amount of reagent (parts per million of aluminum sulfate) required to produce a visible floc within fifteen minutes after reagent addition. All flocculation values were determined in low form, 100 milliliter graduated cylinders.

Initially, considerable difficulty was encountered in reproducing flocculation values on control samples. The problem was resolved, in part, as familiarity with the test itself improved. However, to obtain completely acceptable duplication of values, it became necessary to incorporate into the test procedure a standard method of stirring all samples just prior to beginning the timed period of floc growth. The standard method employed consisted of agitating the samples by the vigorous reciprocating action of a perforated disc approximately 0.5 inches smaller in diameter than the cylinder.

Samples were irradiated in stoppered test tubes. Like samples were combined after irradiation for the determination of flocculation value. Irradiation was performed at dose rates ranging from 117 to 950 rads per minute. Total doses ranging from 5,400 to 100,000 rads were accumulated.

FIGURE 12
VARIATION OF FLOCCULATION VALUE IN IRRADIATED BENTONITE SOLS

Figure 12 is typical of the data obtained during the study. Beyond approximately 30,000 rads, increases in flocculation value as high as +20 to +30 percent were routinely observed. In no case were decreases in flocculation value observed after total doses of approximately 20,000 rads were accumulated. The oscillatory nature of the data is not completely understood, although some indeterminate fraction of the effect is undoubtedly due to differences in stock suspensions. However, decreases in flocculation value at lower total doses were repeatedly observed, and there is no question that the decrease in stability of the suspensions was real. The maxima and minima were not totally reproducible, however, either in regard to magnitude or point of occurrence in terms of total absorbed dose. Thus there is question whether the changes were entirely due to an effect of radiation on the bentonite itself. None of the shifts described appeared to be related to dose rate, since a similar pattern was observed with samples irradiated at rates ranging from 117 to 950 rads per minute.

Dynamic Irradiation Tests. Stock suspensions of bentonite were prepared and assayed for total solids and hydrogen ion concentration as previously described. The effect of ionizing radiation on these suspensions was studied by comparing responses to flocculating agents before and after exposure to a gamma flux. The flocculating agents employed were aluminum sulfate (alum) $[Al_2(SO_4)_3]$, ferric sulfate $[Fe_2(SO_4)_3]$, ferrous sulfate $[Fe(SO_4)]$ and three organics, Nalco 600, 670 and 672 (Nalco Chemical Company).

All reagents were added to the suspensions as aqueous solutions. The effect of adding the reagents prior and subsequent to irradiation was also studied. Irradiations were performed in low form, 100 milliliter graduated cylinders while the samples were under agitation with the apparatus described previously.

No effort was made to assign discrete flocculation values during this phase of the study. Instead, after undergoing an agitation cycle (15 minutes at 55 rpm followed immediately by 15 additional minutes at 10 rpm), all samples were allowed to settle undisturbed for 15 minutes. At the end of that period, the top 5 milliliters of the suspension were carefully removed, and the concentration of bentonite was estimated by the turbidimetric procedure already described. The percentage of total solids still in suspension was assumed to be directly related to the stability of the sol under study.

To preclude the introduction of new variables and to standardize the conditions of the investigation, irradiation time was limited to 30 minutes, the duration of one agitation cycle. A dose rate of 950 rads per minute was the maximum available. Consequently, the data obtained during this phase of the study was limited to total doses of 28,500 rads or less.

As previously noted, bentonite sols prepared from the same lot of dry material are typically subject to considerable variability in basic character. Some portion of the variability can be ascribed to differences in the hydration of the mineral just prior to suspension, the pH of the suspending medium, total solids,

and particle size distribution. Sols from which the following data was obtained were subject to this variability. Although measurements between samples taken from one stock solution were reproducible with a precision of at least ± 10 percent, the range observed between samples taken from different stock suspensions was considerably greater. Variations encountered are tabulated below.

<u>Variable</u>	<u>Range</u>	<u>Average</u>
percent solids	490-385 ppm.	400 ppm
pH	8.5-6.9 **	8.1
Estimated flocculation value with alum	19-12 ppm.	14

**The pH and the resistivity of the distilled water used as a suspending medium were 6.2 ± 03 and 8.5×10^5 (or more) ohms/cm, respectively.

This variability was taken into account when planning experimental series which involved the comparison of data in terms of dose rate dependency, concentrations, total dose effectiveness, etc. In all cases where such comparisons are made in the following pages, the data was obtained using samples taken from the same stock suspension.

Clarification with Inorganic Flocculants. Samples of a bentonite sol were irradiated with approximate total doses of 2,500, 3,750, 5,700, 7,200, 9,000, 11,250, 14,250, 17,500, 21,000, 22,500 and 28,500 rads. Irradiations were performed at dose rates of 232, 291, 415, 586 and/or 950 rads per minute. Prior to irradiation, the samples were treated with aluminum sulfate in concentrations

FIGURE 13
EFFECTS OF RADIATION ON FLOCCULATION OF BENTONITE WITH ALUM

of 15, 16, 17 or 18 parts per million. The samples were irradiated under agitation. Upon completion of the agitation cycle and following a 15 minute quiescent settling period, assay of the solids remaining in suspension indicated a definite increase in sol stability after irradiation. The more salient features of the data obtained are tabulated below, and the complete results of the study are presented graphically in Figure 13.

Total Absorbed Dose	Percent solids remaining in suspension after treatment with alum concentration			
	Alum Concentration			
	15 ppm	16 ppm	17 ppm	18 ppm
0 Rad	100%	58	32	0
2,500 Rad	100	64	40	2
11,250 Rad	100	81	42	8
28,500 Rad	100	82	45	8

The phenomenon did not appear to be dose rate dependent. Repeated experimentation on other stock suspensions indicated that the data given in the referenced figure is typical, and that, invariably, irradiation of a bentonite sol within the limits studied increased the stability of the sol to flocculation with aluminum sulfate.

When the alum was added after the irradiation was completed, clarification of both irradiated and control sols was less efficient, undoubtedly because of the shorter time period available for floc growth. However, in all cases, irradiated sols

FIGURE 14

COMPARATIVE EFFECTS OF RADIATION ON BENTONITE SOLS FLOCCULATED WITH ALUMINUM AND FERRIC SULFATES

were more stable than the corresponding controls. Again, there appeared to be no dependence on dose rate.

Samples of bentonite sol were treated with varying concentrations of aluminum or ferric sulfate and irradiated with 7,500 rads at 250 and 586 rads per minute. The solids remaining in suspension in irradiated and in control samples are plotted against concentration of the flocculating agent in Figure 14. Typically, the irradiated sols were resistant to flocculation with aluminum sulfate. Treatment of irradiated sols with ferric sulfate resulted in a considerably different picture. The causes for the flexion in the curve are not at all clear, but repeated experimentation confirmed the data, and there is no question that the flexion is real. There was no apparent dependence upon dose rate.

Irradiation of samples of bentonite sol pretreated with ferrous sulfate resulted in the data presented in Figure 15. It was anticipated that the radiation induced oxidation of ferrous ion to the more powerful flocculant ferric ion would cause a substantial decrease in sol stability, and that the undulant pattern shown in Figure 15 would be present. The decrease in sol stability occurred, but the pattern typical of treating irradiation sols with ferric ion was absent. This pattern difference was due to the relatively slow formation of FeIII by radiooxidation of FeII compound, as compared with its more rapid addition to irradiated sols.

FIGURE 15

EFFECTS OF RADIATION ON FLOCCULATION OF BENTONITE SOLS WITH FERROUS SULFATE

The effects of adding the ferrous ion flocculant before and after irradiation were compared. The total absorbed dose was kept low to maintain a constant floc time growth. Data obtained from the experiment is shown in Figure 15. Again, the radiation induced oxidation of ferrous ion caused a sharp decrease in sol stability. The increased stability of suspensions treated with flocculant after irradiation was presumed to be analogous to the increases observed when irradiated sols are treated with aluminum sulfate.

Effects of Sugar Impurity. To speed the acquisition of data, tablets of flocculating reagents were formed using a sucrose binder and a device which permitted introduction of the tablets into the suspensions with the sample tray already in radiation position. The data obtained from these initial experiments indicated that irradiation of suspensions treated in this way resulted in sharp decreases in sol stability rather than increases as expected.

Study showed that the presence of sucrose was causing the decrease. When increasing amounts of sucrose were added to bentonite sols and the sols were irradiated with 7,500 rads, the curves shown in Figure 16 were obtained. This information clearly indicated that, in the presence of sucrose, radiation decreased the resistance of bentonite sols to flocculation with aluminum sulfate.

FIGURE 16
EFFECTS OF INCREASING SUCROSE CONCENTRATIONS
ON IRRADIATED AND CONTROL BENTONITE SUSPENSIONS

The action of the sucrose was not clear from the data obtained in the study, although it appeared from the irregular shape of the curve that two, or perhaps three, separate mechanisms were operative. Tests for reducing sugars in the supernatants of the irradiated sols were negative with both Fehling's and Benedict's solutions. There was no significant change in the pH of the sols after irradiation.

Further investigation resulted in the data plotted in Figure 17. Again, the presence of sucrose caused a reduction in the stability of irradiated sols. There was no evidence that the phenomenon was dose rate dependent.

Clarification With Organic Flocculants. Bentonite suspensions were pre-treated with a quantity of aluminum sulfate insufficient to cause flocculation, and with increasing amounts of a cationic organic flocculating aid (Nalco 600, Nalco Chemical Company, Chicago, Illinois). As anticipated, after irradiation, the effectiveness of the organic was decreased (Figure 18). The reduction in effectiveness of the organic (tentatively assumed to be due to radiation decomposition as well as an increase in sol stability) was particularly evident when it alone was used to flocculate the suspensions (Figure 18). Similar results were obtained when irradiated Nalco 600 was used to flocculate unirradiated bentonite, confirming the supposition that radiation decomposition was one of the principal causes for the reduced effectiveness of the organic agent.

FIGURE 17

EFFECTS OF SUCROSE ON FLOCCULATION OF BENTONITE SOLS

FIGURE 18
EFFECTS OF RADIATION ON AN ORGANIC FLOCCULATING AID

Conclusions. Exposure to ionizing radiation results in changes in the basic properties of a model aqueous colloid system. The most significant change in those properties studied was the relative stability of irradiated sols. In a "pure" system, irradiation increased the stability of the suspension to flocculation by alum. In the presence of sucrose, however, the relative stability of the suspensions was decreased. These changes in sol stability were observed after exposure to relatively low (less than 10^3 Rad) total doses.

The data indicates that it is possible to increase the sedimentation rate of an aqueous colloidal suspension and reaffirms previous work⁶ suggestion that this phenomenon may have application to water treatment problems. It is necessary to irradiate the suspensions in the presence of the flocculating agent to obtain this decreased stability, however, and the data shows that organic flocculants are ineffective after irradiation, presumably because of the radiation damage incurred.

(6) AEC Report No. COO-275: *Investigation of the Effects of Ionizing Radiation on Synthetic Detergents, Sewage Colloidal Characteristics and Sewage Sedimentation* (UMC Document D63-341, 6 September 1965).

NOTE: A 1:1 (v/v) mixture of light mineral oil and distilled H₂O was mixed during irradiation at 950 rads/minute. The emulsion volume at the end of mixing and irradiation was compared to that for an unirradiated control sample.

FIGURE 19
EFFECT OF IRRADIATION ON EMULSION STABILITY

IRRADIATION OF NATURAL OILS AND EMULSIONS

Introduction. These experiments were undertaken to study three facets of radiation effects on oil-water emulsions:

- (1) Emulsion formation without surfactants
- (2) Viscosity changes of natural oils
- (3) Separation of surfactant stabilized emulsions

Radiation-Induced Emulsion Formation. To determine if irradiation during mixing would result in stable aqueous emulsions, mineral oil, peanut oil, olive oil and tall oil were mixed (Waring blender, ca. 8,000 rpm) with equal volumes of distilled water. During the mixing process, samples were irradiated at 950 rads per minute. After irradiation and mixing, the volumes of the oil, water and emulsion phases were measured and compared with unirradiated control samples. Exposure to a total dose of 17×10^3 rads resulted in an approximate increase of two-fold in emulsion volume relative to control values 24 hours after mixing. Figure 19 shows the volume of mineral oil emulsions plotted against time. Irradiation of the oil and the water separately with a dose of 53×10^3 rads prior to mixing had no observable effect on emulsion stability.

Emulsion stabilization similar to that shown in Figure 19 was achieved with all the oils tested. These data indicate that water radical interaction at the oil interface is necessary for the formation of emulsion stabilizing functional groups.

Oil Viscosity Changes Due to Irradiation. The oils listed in the table below were irradiated with the total doses indicated. Viscosities were then determined with a #400 Ostwald-Cannon-Fenske viscometer. In all cases the dose rate was 950 rads per minute.

<u>Sample</u>	<u>Viscosity in Seconds</u>		
	<u>Unirradiated Control</u>	<u>57,000 Rads</u>	<u>171,000 Rads</u>
Mineral Oil (85-95)	28.2 (27.8-28.8)	26.9 (26.6-27.8)	
Mineral Oil (145-155)	54.8 (52.6-56.4)	56.5 (52.5-59.6)	53.3 (52.0-54.9)
Peanut Oil	101.5 (97.2-107.0)	106.6 (103.1-109.4)	98.9 (95.5-102.9)
Olive Oil	64.7 (62.8-66.4)	69.4 (68.5-70.0)	58.9 (56.5-60.0)
Paraffin Oil	22.0 (19.8-22.2)	22.2 (22.2)	19.9 (19.2-20.5)

IRRADIATION EFFECT ON OIL VISCOSITIES

NOTE: The viscometry data represent the mean of five determinations. The range is given in parentheses below each mean.

The data indicated that the direct effects of radiation are more pronounced in the triglyceride oils than those of hydrocarbon origin. This observation confirms the data in the previous section, which showed that the triglycides tended to

Note: Emulsification was by waring blender during irradiation

FIGURE 20
THE EFFECT OF IRRADIATION ON EMULSION STABILITY
OF 1:1 WATER AND MINERAL OIL WITH TWO EMULSIFYING AGENTS

form more stable emulsions upon irradiation. The ranges of the measurements taken, however, are quite wide, and in several cases, the coincidence of the values observed prohibit assigning quantitative significance to all of the data.

Irradiation Separation of Surfactant-Stabilized Emulsions.

Emulsions of mineral oil and water (1:1) were prepared by standard methods using 0.025 to 0.20 percent (w/v) of the following surfactants as emulsifiers:

- (1) Non-ionic - (Non-ion-ox)
- (2) Anionic
 - a. Alkylaryl Sulfonates (AAS) - Alkyl Benzene Sulfonate (standard) and Sparkleen
 - b. Alkyl Sulfates (AS) - Sodium Dodecyl Sulfate

A portion of each emulsion was irradiated at 586 rads per minute, while the remainder served as the unirradiated control. After exposure to a total dose of 4×10^5 rads, emulsions prepared with non-ionic and AS surfactants had separated, but those prepared with AAS detergent had not broken.

Figure 20 shows the effects of emulsions stabilized with Sparkleen (AAS-Type) and Non-ion-ox (non-ionic type) after exposure to 1.4×10^4 rads at a dose rate of 586 rads per minute. Emulsification was carried out during irradiation.

The emulsions prepared with Sparkleen differed from unirradiated controls. Those prepared with Non-ion-ox varied only during the initial 8 to 9 minutes.

Irradiation doses of 4×10^5 rads at 950 rads per minute produced interesting results on surface tension of aqueous solutions of the three detergents. The surface tension of 0.025 to 0.05 percent (w/v) alkylbenzene sulfonate (25 or 50 mg. ABS/100 ml of water) increased after irradiation. Further irradiation, however, produced the opposite effect, and decreases were invariably observed. Sodium dodecyl sulfate solutions of similar concentrations, however, exhibited little change in surface tension after exposure to a similar total dose. The surface tension of Non-Ion-Ox solutions of similar concentration decreased progressively with increasing dose.

Conclusions. These data indicate that surfactant-free oil and water emulsions can be stabilized by irradiation. The stabilization occurs only when emulsification and irradiation are performed simultaneously, suggesting that a hydrophilic site is formed on one end of the oil molecule by reaction with radiolytic products in the water. This attack would be nil in separated oil and water. The pattern of viscosity changes observed in irradiated oils supported this hypotheses.

The potential industrial applications of radiation for the control of emulsion stabilities would seem to be greatest in the insecticide, paint, pharmaceutical and chemical industries.

SPAN-1, 4-SORBITAN FATTY ACID MONO ESTER*

TWEEN-POLYOXYETHYLENE 1,4-SORBITAN MONOESTER*

*The triester would be formed by reaction with the alcohols on carbons 3 and 5

FIGURE 21
SURFACTANT STRUCTURAL FORMULAE

NON-IONIC SURFACTANTS

Introduction. There were over 3,000 surface active agents available commercially in the United States as of 1960. To a considerable extent, this multiplicity of products represents the marketing of identical or substantially identical products by various suppliers under a variety of trade names. These agents are used singly or in blends as emulsifiers in a wide variety of products, and annual sales are on the order of several million dollars. Despite their numbers, however, and broad range of properties in which they are available; there are many processing problems associated with their use. Among these are difficulties with the preparation of several types of emulsions and the *in situ* alteration of the surfactant's characteristics.

Span, Tween and Tergitol are proprietary names for typical non-ionic detergents. The first two are products of Altas Chemical Co., and the latter of Union Carbide Corporation. Span surfactants are complex fatty acid esters of 1,4-sorbitan, and Tween surfactants are polyoxyethylene substituted sorbitans esterified with fatty acids. Structural formulae for these detergents are presented in Figure 21. The Tergitols are esters of polyoxyethylene and various aromatic or aliphatic hydrocarbons. The profound changes observed in polyoxyethylene and the well documented liability of ester linkages to radiolysis⁷ suggested

(7) A. O. Allen, *Radiation Chemistry of Water and Aqueous Solutions* (New York, 1961).

SOLVENT FRONT

ORIGIN

FIGURE 22
THIN-LAYER CHROMATOGRAM OF IRRADIATED
AND CONTROL SURFACTANTS

that surfactants containing these moieties would also be subject to radiation induced changes in their emulsifying properties. Consequently, preliminary study of the effects of radiation on these materials was undertaken.

Experimentation. Samples of seven detergents were obtained for the study. These were:

- (1) Tween 80 - polyoxyethylene (20) sorbitan monooleate
- (2) Tween 85 - polyoxyethylene (20) sorbitan trioleate
- (3) Tween 81 - polyoxyethylene (5) sorbitan monooleate
- (4) Span 20 - sorbitan monolaurate
- (5) Span 40 - sorbitan monopalmitate
- (6) Span 60 - sorbitan monostearate
- (7) Tergitol NP-27 - polyoxyethylene (7) nonylphenyl ether

NOTE: In Figure 22 the numbers above are used instead of proper names for purposes of brevity.

Span and Tween surfactants are amber oily liquids, usually containing less than 5 percent water. To simplify subsequent analytical procedures during these preliminary studies, these materials were irradiated as supplied by the manufacturer. Tergitol NP-27 is a white powder. It was prepared in a 1 ppm aqueous solution.

Samples of Tween and Span surfactants were exposed to total doses of 10.3×10^6 rads. Tergitol solutions were exposed to

total doses of 10^5 rads. In all cases, the dose rate was 935 rads per minute and the irradiations were performed in the 8,000 curie cobalt-60 facility described previously.

The effects of radiation on Tergitol were measured by comparing pH, surface tension, and foaming potential of irradiated solutions with similar values in control solutions. The pH values were determined with a Beckman Model 1019 pH meter and standard buffers. Surface tension was estimated by measuring the differential of equilibrium liquid heights in a #50 Ostwald-Cannon-Fenske standard viscometer. Foaming potential was assumed to be related to the height of the separated column of foam (air/liquid interface) specified time intervals after a standardized mixing procedure.

The effects of radiation on Tween and Span surfactants were evaluated by comparing control and irradiated samples using thin layer chromatographic techniques (TLC), classical spot testing procedures, and Hydrophile-Lipophile Balance (HLB), a systematic scheme devised by the manufacturer for characterizing the detergents.

- TLC Tests - Conventional absorption TLC was performed on irradiated and control samples using silica gel plates and appropriate developing solvents. The separated components on the chromatograms were located by:

- (1) Illumination with ultra violet light .
- (2) Iodine vapor nucleation techniques
- (3) Sulfuric acid char methods
- (4) Reactivity with phosphomolybdic acid reagent

In general the best detection of resolved spots was obtained with iodine vapor and with the phosphomolybdate reagent.

- Spot Tests - Classical spot tests were performed on 20 to 100 milligram samples of surfactants applied onto silica gel plates similar to those used in TLC. The spot test reagents were sprayed onto the plates, and the color changes were observed in normal room light. The reagents employed were:

<u>Compound Detected</u>	<u>Reagent</u>	<u>Indications</u>
Carbohydrates	(1) anisaldehyde - sulfuric acid	- -
	(2) naphtholresorcinol - phosphoric acid	- -
Carboxylic Acids	Bromcresol Green in sodium hydroxide	yellow below pH 4.0
Lipids	Bromthymol Blue in sodium hydroxide	- -
Carbonyls	2,4 dinitrophenylhydrazine (2, 4-DNPH)	aliphatic-yellow aromatic-red
Esters	hydroxylamine - ferric ion	- -
Reducing Compounds	(1) phosphomolybdic acid	- -
	(2) blue tetrazolium	- -
Conjugated Olefinic Bonds	ultraviolet illumination	non-specific locator
Surface Activity	water spray	relative test

- HLB Tests - The Hydrophile Lipophile Balance (HLB) test is a means of determining the emulsifying power of surfactants. It was developed by the Atlas Chemical Co. (booklet #LD-97-RI-6M-9-64) specifically to characterize the type of surfactants studied. Ancillary data such as emulsion locus, oil volume and emulsion type was also recorded. The tests were conducted as follows:
- a. Blend 0.5 milliliter of surfactant or the equivalent amount of solid surfactant with 10 milliliters of the oil phase (e.g. benzene, kerosene, etc.).
 - b. Add 39.5 milliliters of distilled water, and mix by inverting 20 times.
 - c. Start the interval timer, and record the lapsed time until an interface appears.
 - d. End the experiment when two phases appear in all samples of the series, or at a predetermined time interval.
 - e. For each sample, record:
 - (1) Volumes of oil phase and the emulsion
 - (2) Location of the emulsion (i.e. in the oil, the water or at the interface)
 - (3) Emulsion type

For the experiments described in this document, the end point for the test was defined as the time interval required for the emulsion to break in all samples, except one in the series. A typical test series consisted of

eight graduated cylinders, each containing emulsions prepared from the standard amounts of surfactant, distilled water, and one of the "oils" standardized by Atlas for this purpose. The standard oils used in the HLB series were:

<u>OIL</u>	<u>HLB</u>
Cottonseed oil	6
Paraffinic mineral oil	10
Bromobenzene	13
Ethyl Benzoate	13
Kerosene	14
p-Diisopropylbenzene	15
Toluene	15
Carbon tetrachloride	16

Tergitol NP-27 Results. After irradiation (10^5 rads), solutions of Tergitol were compared to controls with respect to relative surface tension, pH and foaming potential. No differences in surface tension beyond the limits of experimental error were observed between irradiated and control samples. In all cases, however, the pH of irradiated solutions was approximately 0.5 units higher than control values. The pH of control solutions was always approximately 4.0. After 5 minutes, the height of the foam column remaining over control solutions was always in the range of 1.0 to 2.0 centimeters. No foam remained over irradiated solutions after a similar time.

FIGURE 23
FACSIMILE THIN-LAYER CHROMATOGRAM OF
IRRADIATED AND CONTROL SURFACTANTS

⊗ = Spots reacting with I_2 vapor

⊙ = Spots reacting with I_2 vapor and phosphomolybdic acid

Tween and Span Results.

- Thin Lay Chromatography - Figure 22 presents a photograph of a thin layer chromatogram typical of those developed during the study. The developing solvent was of relatively low elutropic strength and consisted of 90:10:10 (parts by volume) of benzene: methanol: carbon tetrachloride. The distance between the origin (O) and the solvent front (s.f.) was 27.0 centimeters, and development was performed by ascending technique. The developed chromatogram was visualized by nucleation with iodine vapor. Primed numbers indicate lanes containing irradiated (10.3×10^6 rad) surfactants. Unprimed numbers indicate lanes containing control samples.

Figure 23 presents a facsimile of chromatogram developed in a more elutropic solvent (benzene: methanol: carbon tetrachloride: water in 80:15:15:1 parts by volume) in order to separate more polar components. Sample lanes are designated by the same system described above, and the distance from origin (O) to solvent front (s.f.) was 16.5 cm. Because of the difference in elutropic strength of the solvents employed, spots located at the middle and some of those at the origin in Figure 22 will be found at the solvent front and middle, respectively, of Figure 23.

In general, the more mobile the fraction, the lower its polarity. Fractions remaining at or near the origin in either solvent mixture are, most probably, highly polar

lipids and/or carbohydrates. There was a remarkable similarity in the chromatographic qualities of control surfactants within the same family, i.e., there was little chromatographic differentiation of any one control Tween sample from another, or one control Span sample from another. The principal distinguishing characteristics observed were the presence, absence, or dislocation of single spots. As anticipated because of their relative complexity, control samples of the Tween surfactants separated into a greater number of components than the Spans.

Study of Figure 22 indicates that, chromatographically, there was little radiation induced change in any Span sample except for the lower R_f value of the leading (non-polar) fraction of Span 20. The spot patterns observed in Figure 23 confirm this indication. With the exception of the disappearance of a mobile, non-polar, reducing fraction from irradiated samples of Span 40 and 60, and the appearance of a non-reducing fraction of intermediate polarity in irradiated Span 40, controls and irradiated samples of these surfactants were chromatographically similar. Irradiated samples of Span 20, however, substantially differed from their controls. The principal differences were:

- (1) The appearance of a polar reducing fraction which remained at the origin in irradiated samples

- (2) Radiation-induced loss of reducing properties in three fractions of intermediate polarity
- (3) Radiation induced appearance of a reducing fraction of intermediate polarity

Figure 22 further indicates that there were substantial radiation-induced changes in all samples of Tween. This indication is confirmed by examination of Figure 23. Again, the principle changes observed between irradiated and control samples were confined to the more mobile, less polar components. The sole radiation-induced changes observed in the lower portion of the chromatogram were the appearance of a single, non-reducing component of low intermediate polarity in Tween 80 (1') and in Tween 81 (3').

The chromatographic changes in the s.f. portions of the chromatograms are considerable for all Tween samples, however, and involve:

- (1) Appearance of a non-polar, non-reducing band at the solvent front
- (2) Appearance of another reducing fraction of high polarity with the same approximate R_f as that observed in control samples
- (3) Either the coalescence of three non-reducing fractions of intermediate polarity into a single component, or the disappearance of two fractions of this type

TEST	SURFACTANT											
	Tweens				Spans							
	80		85		81		20		40		60	
	I	C	I	C	I	C	I	C	I	C	I	C
Anisaldehyde - H ₂ SO ₄	b	b	b	b	v	v	wpk	wpk	wpk	wpk	wpk	wpk
Naphthoresorcinol - H ₃ PO ₄	y	-	y	-	wb	-	wb	-	b	-	b	-
Bromothymol blue - NaOH	y	y	y	y	y	y	y	y	-	-	-	-
2, 4-DNPH	y	y	y	y	y	y	y	y	wy	-	sy	-
Hydroxylamine - Fe ⁺³	-	-	r	r	-	wr	sr	sr	wr	wr	wr	wr
Phosphomolybdic acid	-	-	b	b	b	b	b	wb	b	wb	b	-
Blue Tetrazolium	wr	-	p	-	p	-	r	-	sr	-	sr	-
Bromocresol green - NaOH	wy	wy	wy	wy	wy	wy	y	y	-	-	-	-

Results of Spot Tests

NOTES:

CHEMICAL REACTIVITY OF DETERGENTS

- Spot Tests - Both irradiated and control samples (20 to 100 mg.) of each surfactant were spotted on standard silica gel plates similar to those used in TLC. The spotted samples were then tested for their reactivity to the reagents already described. Test reagents were sprayed onto the plates by standard techniques, and the colors were sprayed onto the plates by standard techniques. Colors produced were evaluated in normal room light. The data obtained is tabulated below and on the opposite page.

<u>Groups Tested For</u>	SURFACTANT											
	<u>Tweens</u>						<u>Spans</u>					
	80 I	80 C	85 I	85 C	81 I	81 C	20 I	20 C	40 I	40 C	60 I	60 C
Carbohydrates - (Anisaldehyde - H_2SO_4) (Naphthoresorcinol - H_3PO_4)	2+	2+	2+	2+	2+	2+	+	+	+	+	+	+
	2+	0	2+	0	+	0	+	0	2+	0	2+	0
Acids - (Bromcresol Green)	+	+	+	+	+	+	2+	2+	0	0	0	0
Lipids - (Bromthymol Blue)	2+	2+	2+	2+	2+	2+	2+	2+	0	0	0	0
Carbonyl Groups - (2, 4-DNPH)	2+	2+	2+	2+	2+	2+	2+	2+	+	0	3+	0
Esters - (Hydroxylamine)	0	0	2+	2+	0	+	3+	3+	+	+	+	+
Reductants - (Phosphomolybdic acid) (Blue Tetrazolium)	0	0	2+	2+	2+	2+	2+	+	2+	+	2+	0
	+	0	2+	0	2+	0	2+	0	3+	0	3+	0
Conjugated olefinic bonds	3+	3+	3+	3+	3+	3+	3+	3+	3+	3+	3	3+
Surface Activity	3+	3+	3+	3+	3+	3+	+	+	+	+	+	+

RELATIVE AMOUNTS/ OF CHEMICAL TYPES OR GROUPS AS FOUND

BY SPOT TESTS OF CONTROL AND IRRADIATED SURFACTANTS

Abbreviations and Symbols:

0 - negative test within detection limits (7)	3+ - strong reaction
+	- weak reaction
2+ - medium strength reaction	I - Irradiated (1.03×10^7 rad)
	C - Controls

Study of these data will show that, following irradiation:

- a. There was an increased reactivity to the naphtholresorcinol - phosphoric acid reagent in all samples, but no change in response to the anisaldehyde-sulfuric acid reagent.
- b. All Span surfactants exhibited a marked increase in reactivity to both the phosphomolybdic acid and blue tetrazolium tests for reducing agents.
- c. All Tween surfactants exhibited an increase in reactivity to the blue tetrazolium reagent but not to phosphomolybdic acid.
- d. Samples of Tween 81 no longer exhibited a positive test for ester linkages.
- e. There was a strong increase in the apparent concentration of carbonyl groups in samples of Span 60 and a slight increase in samples of Span 40. There was no change in samples of Span 20.

As already noted, Span surfactants are fatty acid esters of 1,4-sorbitan and Tweens fatty acid esters of polyoxyethylene substituted sorbitan. There is no claim made by the vendor regarding the purity of these preparations. Each surfactant, as supplied, is composed of a more or less constant spectrum of chemical moieties which determine its surface active properties. The heterogeneity

FIGURE 24

RADIATION INDUCED HLB CHANGES

of the preparations precludes definitive comment on the meaning of the changes noted in reactivity to the spot tests performed. Tentatively, however, it is possible to suggest that:

- a. Cleavage of polyethylene glychol chain in Tweens seems important.
- b. Oxidation is the principal reaction mode by which the radiation induced changes occur.
- c. There is radiolytic attack on the ester linkages, although this is probably not one of the chief reactions.
- d. The most likely sites at which the radiooxidation occurs are the unsubstituted hydroxyl groups on the sorbitan nucleus, the acetal linkage in the sorbitan nucleus, and the ester linkage.

● HLB Determinations - Figure 24 presents histograms of a portion of the HLB data acquired during the studies described herein. The results over the entire range of HLB studied (6 to 16) are shown for Span 40 and Span 60. The data plotted is restricted to ranges of HLB between 10 and 16 (Tween 80 and Span 20) or 12 and 16 (Tween 81 and Tween 85), since there were no differences in the histograms outside of these values.

There are significant differences in the observed HLB values of control and irradiated samples of all surfactants except Tween 85. The differences consisted principally of either

shifts of HLB (Tween 80 and Tween 81) or the appearance of additional HLB peaks (Span 20, 40 and 60) with little or no change in the original values. There may be a correlation between the new HLB values observed in the Span samples and the radiation induced reactivity with the phosphomolybdic acid reagent for reductants. No such straight forward relation between spot test and HLB data was noted for Tween samples.

Conclusions. The studies performed thus far unequivocally show that it is possible to induce functional (HLB) change in certain non-ionic detergents by exposure to gamma radiation. The effects which will be induced in dilute aqueous solutions are unknown, since the preliminary investigations were performed on the undiluted surfactants.

For the modification of surfactant properties on a commercial scale, it is obvious that radiation treatment of the highly concentrated material is preferable to irradiation of dilute aqueous solutions. Irradiation provides the manufacturer of surfactants with another tool for precise "tailoring " of the product to specific requirements.

There is no immediately obvious and firm correlation between the shifts in HLB observed and the results of thin layer chromatography and spot test analysis. Further studies should include the use of developing solvents of greater elutropic strength, spot tests

of improved sensitivity and selectivity, and instrumental analysis of separated components. These will permit better definition of the magnitude and nature of the chemical changes induced. This study will be greatly facilitated by separation of the technical products into their purified components.

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